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(54) Title of invention

An apparatus of detecting traces of gas

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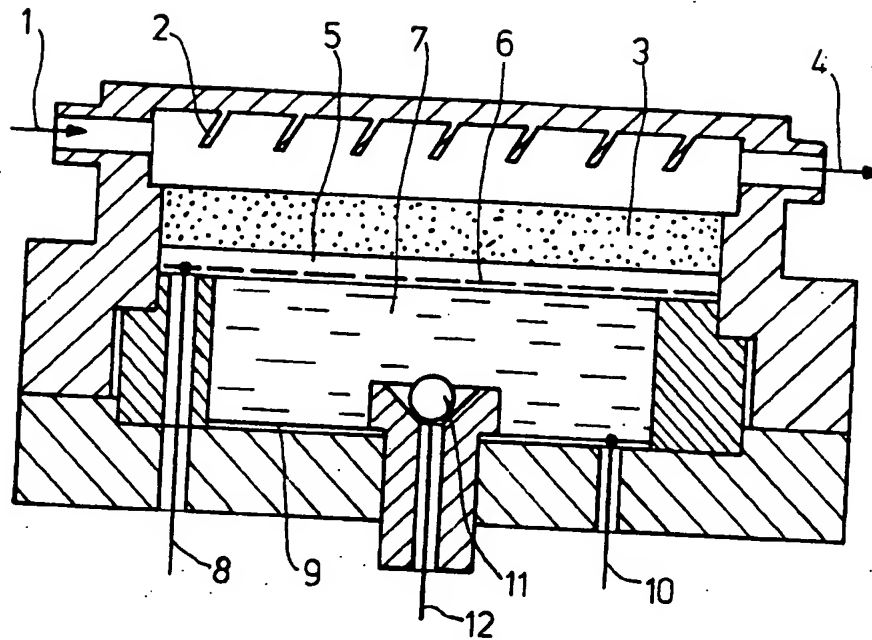


FIG. 1

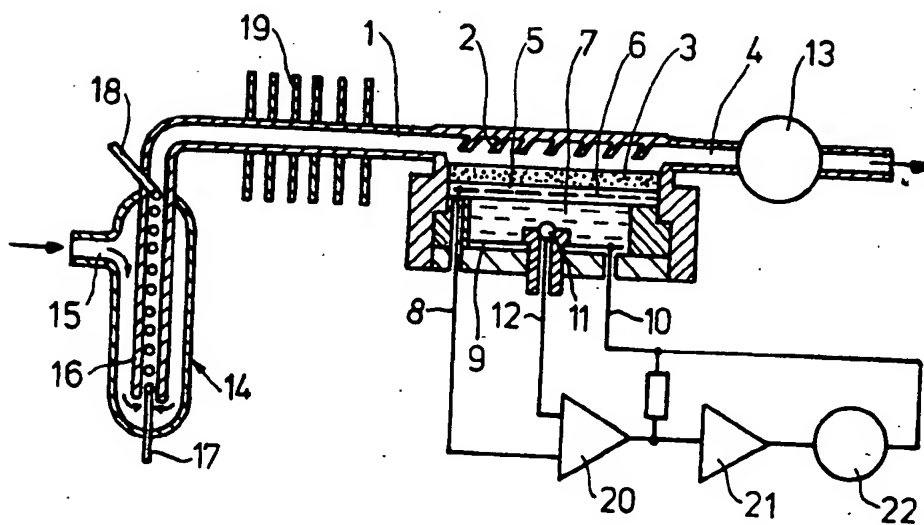


FIG. 2

## SPECIFICATION

## An apparatus for detecting traces of gas

The present invention relates to an apparatus for detecting traces of nitrogen dioxide in a gaseous mixture, comprising an electro-chemical cell with a working electrode, reference electrode and auxiliary electrode in an organic electrolyte, the working electrode being a polarisable, ion-selective electrode, and also a power source of constant voltage (potentiostat) and a current measuring device.

Electro-chemical cells for detecting a gas in a gaseous mixture are particularly important in the field of environmental protection. By using them, it is possible to determine if dangerous gases are present in the air. In particular, they should indicate when predetermined concentrations are exceeded, and they therefore have to be sensitive without requiring servicing and operate in a uniform manner for a relatively long period.

An electro-chemical cell having a polarographic device with an ion-selective electrode as working electrode is described in German Offenlegungsschrift No. 26 27 271. It has now been found that traces of nitrogen dioxide in a gaseous mixture can be measured in an apparatus of this type if the working electrode is a silver electrode cathodically polarised and coated with silver iodide and the auxiliary electrode comprises silver.

According to the present invention there is provided an apparatus for detecting traces of nitrogen dioxide in a gaseous mixture comprising an electro-chemical cell with a working electrode, a reference electrode and an auxiliary electrode in an organic electrolyte, the working electrode being an ion-selective electrode formed by a cathodically polarised silver electrode coated with silver iodide and the auxiliary electrode comprising silver; a potentiostat connected to said three electrodes including an instrument for measuring the cell current.

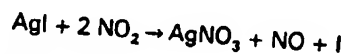
Using an apparatus of this type, other nitrogen-containing gaseous substances can also be detected very sensitively if the cell is preceded by a reactor in which the gas is oxidised by heating and conveyed to the working electrode of the test cell after cooling. Thus embodiments of the present invention provide detection apparatus for acrylonitrile and hydrocyanic acid. According to another embodiment of the invention, acrylonitrile can be measured selectively in addition to hydrocyanic acid. In this embodiment in addition to the apparatus according to the invention for detecting acrylonitrile there is provided a gas detector for detecting hydrocyanic acid, the acrylonitrile concentration being determined from the difference between the two measured values.

The working electrode is an ion-selective electrode, a silver electrode, e.g. silver wire gauze, which is coated with silver iodide, and is polarised as the cathode. The auxiliary electrode is composed of silver and an Ag/AgI electrode is advantageously used as the reference electrode.

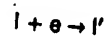
65 The dependence on temperature is greatly reduced by this symmetrical arrangement about the working electrode.

The electrodes are operated in a potentiostat circuit. The electrolyte is an organic concentrated electrolyte. It comprises from 40 to 60%, by weight, diethyl phthalate, from 25 to 35%, by weight, propylene carbonate and from 15 to 20%, by weight, PVC. It also contains means for increasing the conductivity and for stabilising the pH-value.

If nitrogen dioxide is present, iodine is separated at the cathode, but without external current supply in accordance with:



80 As a result of the polarographic process, i.e. the cathodic process



and the anodic process at the auxiliary electrode



85 regeneration of silver iodide takes place, i.e. the working electrode is not attacked, but instead, the auxiliary electrode acts as a sacrificial electrode. This exchange of electrons occurs at an operating voltage of about -140 mV (based on the standard hydrogen electrode).

90 An apparatus according to the invention is illustrated by way of example in the accompanying drawings and is described in more detail below. In the drawings:

95 Figure 1 shows a section through a test cell; Figure 2 shows a test cell with a reactor.

In Figure 1, the gaseous mixture to be examined for nitrogen dioxide enters a test cell at 1. Spiral guiding fins 2 compel a channel above a frit 3 to completely fill. The gas flows out at 4.

100 Gas diffuses into a chamber 5 via the frit 3. This chamber is about 1 mm deep, and the base is covered with a working electrode 6 which, in turn, makes close contact with an electrolyte 7.

105 The working electrode 6 is gauze-like and can be connected to a power source of constant voltage (potentiostat) via 8. The electrolyte 7 is consolidated in a gel form. An auxiliary electrode 9 is composed of silver and is connected to the potentiostat via 10. A reference electrode 11 is composed of silver iodide and connection is made with it via 12.

Figure 2 shows the complete measuring arrangement with a reactor. Reference numerals 115 to 120 have the same meaning as in Fig. 1. A pump 13 (capacity about 20 l/h) sucks the test gas firstly through a micro-reactor 14. The micro-reactor 14 contains a pre-heater 15 and a heating member 16 which is coated with a catalyst. The catalyst is, for example, pyrolusite, and the acrylonitrile is oxidised to carbon dioxide, water and nitrogen dioxide at from 400 to 450°C. The heating member 16, e.g. a platinum wire can be

heated *via* connections 17 and 18. The gaseous mixture is cooled in a cooler 19 and is guided *via* 1 into the test cell. 20 is a potentiostat, 21 a post-amplifier, 25 a display and recording instrument.

- 5 2 ppm nitrogen dioxide produce a primary current of about  $2 \cdot 10^{-8}$  A. The response sensitivity lies below 0.2 ppm; the response time amounts to less than 5 seconds; the zero constant lies at  $\pm 3\%$ ; the 50% time (time until 50% of the final value is attained) amounts to less than 1 minute.

#### CLAIMS

1. An apparatus for detecting traces of nitrogen dioxide in a gaseous mixture comprising an electrochemical cell with a working electrode, a  
15 reference electrode and an auxiliary electrode in an organic electrolyte, the working electrode being an ion-selective formed by a cathodically polarised silver electrode coated with silver iodide and the auxiliary electrode comprising silver; a  
20 potentiostat connected to said three electrodes including an instrument for measuring the cell current.
2. An apparatus according to Claim 1, wherein the electrolyte comprises from 40 to 60%, by  
25 weight, diethyl phthalate, from 25 to 35%, by weight, propylene carbonate, from 15 to 20%, by

weight, polyvinyl chloride and additives to increase the conductivity and the stability of the pH value.

- 30 3. An apparatus according to Claim 1 or 2, wherein a reactor having a catalyst filling is connected upstream of the electro-chemical cell and means are provided for guiding the gaseous stream to be measured, in such a way that the gas  
35 is heated in the reactor and catalytically oxidised and, before it impinges upon the working electrode, flows through a cooling section.

4. An apparatus according to Claim 3, for detecting acrylonitrile.

- 40 5. An apparatus according to Claim 3, for detecting hydrocyanic acid.

6. An apparatus for detecting acrylonitrile with the simultaneous presence of hydrocyanic acid, comprising an apparatus according to Claim 3 and  
45 a gas detector for detecting hydrocyanic acid, wherein the acrylonitrile concentration is determined from the difference between the two measured values.

7. An apparatus for detecting traces of nitrogen  
50 dioxide in a gaseous mixture substantially as herein described with reference to Figure 1 with or without reference to Figure 2 of the accompanying drawings.